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COLOR CENTERS IN POTASSIUM CHLORIDE CRYSTAL CONTAINING SULFATE IONS

By Kiyoshi Shimizu*

Introduction

In the previous paper[1], the author reported that barium ions, as the impurity, being introduced in the potassium chloride crystal, the thermal bleaching of F centers produced electrolytically is accelerated and the formation of the colloid centers is disturbed. It was considered that the rapid bleaching of the F centers in the crystal containing barium ions would be due to the much more decrease of the concentration of the negative ion vacancies during the low temperature heating caused by extra positive ion vacancies accompanied by barium ions.

Now, from the above, it is expected that the divalent negative ions, as the impurity in the potassium chloride crystal, would introduce extra negative ion vacancies for electrostatic balance so that the thermal bleaching of the F centers in this crystal may be retarded. Then, in this experiment, the author has studied the effect of the sulfate ions on the thermal bleaching of the F centers produced electrolytically in the potassium chloride crystal.

Experimentals

The single crystal of KCl containing K_2SO_4 was prepared by Kyropoulos' method. The concentration of SO_4 ions in the crystal was determined by the gravimetry as $BaSO_4$. The procedure was as the same as that in the previous experiments, namely, the coloration of the crystal was performed by means of electrolysis with the pointed cathode of nichrome and the flat anode of graphite in the furnace at 600°C and then quenched rapidly in the air. The specimen for measurements of absorption spectra was cleaved from the inner region of the colored crystal. For the purpose of studying the thermal bleaching of the F centers, the moderately colored specimens were wrapped in the tin-foil and heated at 350~450°C for a definite time. After heating, each specimen was quenched in the air and the absorption spectra of these colored specimens were measured in the wavelength range from 400~1000 mμ at room temperature by means of a Beckman model D U Spectrophotometer. The concentration of the F centers was calculated from Smakula's formula[2].

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1) K. Shimizu, *This Journal*, **28**, 1 (1958)

2) A. Smakula, *Z. Physik*, **59**, 603 (1930)

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Results and Considerations

In the KCl crystal containing SO_4 ions, the F and M bands were produced by electrolysis as well as in the pure crystal, so that the colored specimens were preheated at each temperature in order to obtain the specimens having F centers only and then the investigations were performed on these specimens. As shown in Fig. 1, the bleaching rate of the F centers increased with in-

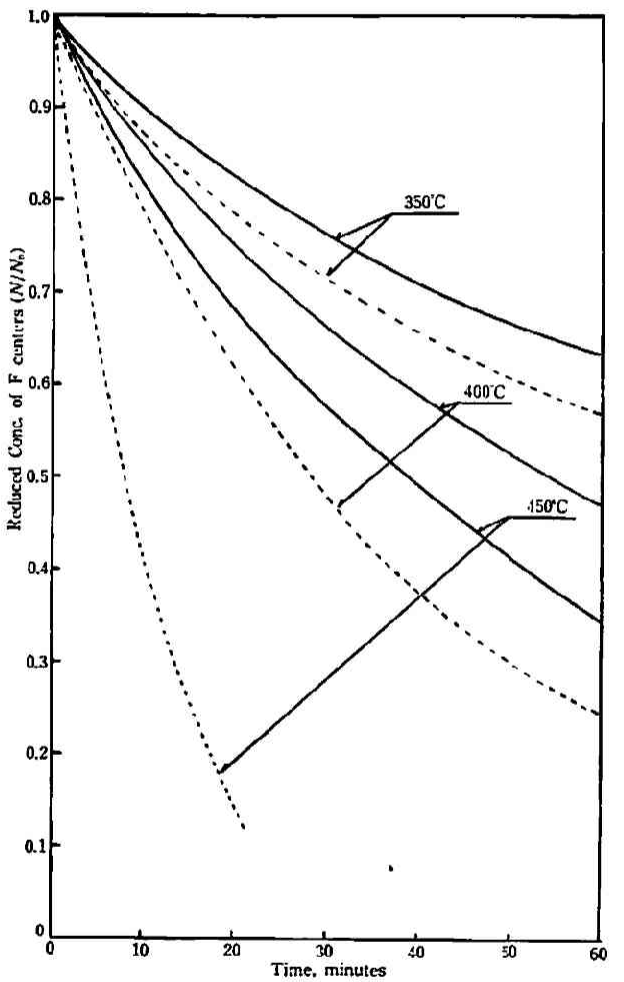

Fig. 1 Thermal bleaching of the F centers in KCl crystal containing 8.2 mole % of SO_4 ions (solid line) and in pure KCl crystal (dotted line)

creasing temperature and decreased with the lapse of heating time at each temperature. The bleaching rate in the specimen of the crystal containing SO_4 ions (solid line) was smaller than that in the pure crystal (dotted line) at corresponding temperature. Plotting the logarithum of the reduced concentration of the F centers, $\log N/N_0$, against the time gives the straight lines as shown in Fig. 2. Therefore, the bleaching of the F centers follows the first order kinetics as in the pure crystal, namely, the bleaching rate of the F centers is proportional to the concentration

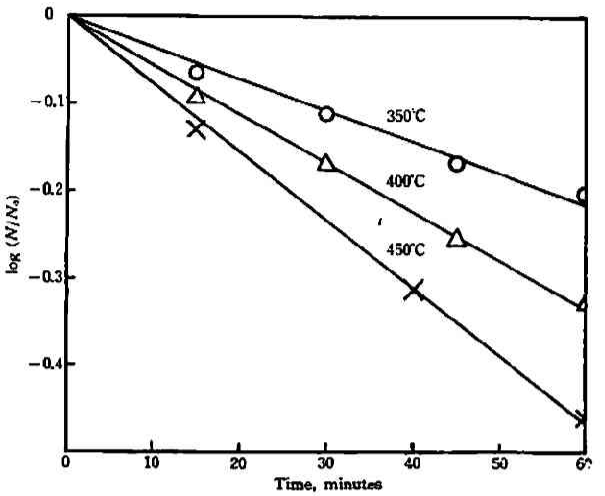

Fig. 2 Relations between $\log (N/N_0)$ (reduced concentration of the F centers) and heating time in the colored specimens of KCl crystal containing 8.2 mole% of SO_4 ions

of the F centers, so the rate determining step would be the process of the migration of the F centers from the inner region of the specimen to the surfaces. But, the apparent activation energy, which has been calculated from the slope of the plots of $\log k_1$ against the reciprocal of the absolute temperature, $1/T$, is about 0.3 eV (Fig. 3). This value corresponds to about a half of that in the pure crystal[1].

In the crystal containing SO_4 ions, SO_4 ions should introduce the extra negative ion vacancies

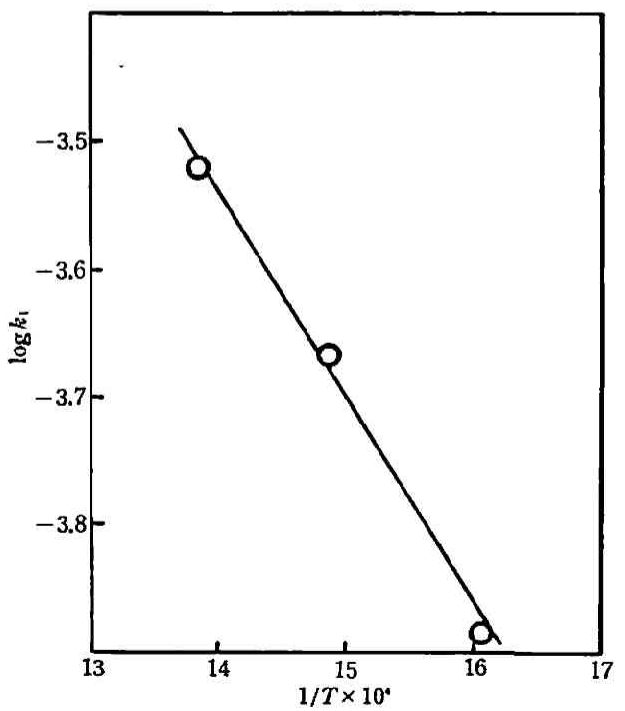

Fig. 3 Relation between $\log k_1$ and $1/T$

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in the crystal at low temperatures for the electrostatic balance and the concentration of the negative ion vacancies in this crystal should be higher than that in the pure crystal so that, during the heating at low temperatures, the decrease of the concentration of the negative ion vacancies in this crystal would be less than that in the pure crystal. From the above considerations, it is concluded that the rate of the bleaching of the F centers in the crystal containing SO_4 ions is smaller than that in the pure crystal because of the retardation of the migration of the F centers.

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